Interestingly, details of the modes of reactions of the various types of metal-centered radicals with alkyl halides appear to differ somewhat from that proposed here for the $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ system; a mechanistic investigation of the latter is underway.[5]

Acknowledgment. Financial assistance from the National Sciences and Engineering Research Council of Canada (operating and equipment grants to M.C.B.) and Alcan International (fellowship to C.A.M.) made this research possible. We also thank M. Koeslag and T. A. Huber for laboratory assistance.

Registry No. $\eta^5\text{-}C_6H_5Cr(CO)_3Br$, 32628-92-5; $\eta^5\text{-}C_5H_5Cr(CO)_3I$, 32628-88-9; $\eta^5\text{-}C_5H_5Cr(CO)_3CH(CO_2Me)_2$, 141685-75-8; $\eta^5\text{-}C_5H_5Cr(CO)_3CH_2CN$, 141685-76-9; $\eta^5\text{-}C_5H_5Cr(CO)_3CH_2CO_2Et$, 141685-77-0; $\eta^5\text{-}C_6H_5Cr(CO)_3CH_2CO_2Me$, 141685-78-1; $\eta^5\text{-}C_5H_5Cr(CO)_3H$, 36495-37-1; $\eta^5\text{-}C_5H_5Cr(CO)_3Me$, 41311-89-1; $\eta^5\text{-}C_5H_5Cr(CO)_3CH_2CH{=}CHCO_2Me$, 141685-79-2; $\eta^5\text{-}C_5H_5Cr(CO)_3CH_2CH{=}CH_2$, 135571-87-8; $\eta^5\text{-}C_5H_5Cr(CO)_3CH_2Ph$, 98316-23-5; $\eta^5\text{-}C_5H_5Cr(CO)_3CH_2CH{=}CHCO_2Et$, 141685-80-5; $\eta^5\text{-}C_5H_5Cr(CO)_3CHMeCO_2Me$, 141685-81-6; $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, 12194-12-6; $BrCH(CO_2Me)_2$, 868-26-8; ICH_2CN, 624-75-9; $BrCH_2CO_2Et$, 105-36-2; $BrCH_2CO_2Me$, 96-32-2; $BrCH_2Ph$, 100-39-0; $BrCH_2CH{=}CHCO_2Me$, 1117-71-1; $BrCH_2CH{=}CH_2$, 106-95-6; $ICH_2CH{=}CH_2$, 556-56-9; ICH_2Ph, 620-05-3; EtI, 75-03-6; Me_2CHI, 75-30-9; Me_3CI, 558-17-8; MeEtCHI, 513-48-4; *n*-BuI, 542-69-8; CH_2I_2, 75-11-6; ICH_2CH_2I, 624-73-7; $ICH_2CH_2CH_2I$, 627-31-6; $I(CH_2)_5I$, 628-77-3; PhCHBrMe, 585-71-7; $BrCMe_2CO_2Et$, 600-00-0; $Br(CH_2)_3CO_2Et$, 2969-81-5; $MeCHBrCO_2Me$, 5445-17-0; $MeCHBrCO_2Et$, 535-11-5; $EtCHBrCO_2Me$, 3196-15-4; $EtCHBrCO_2Et$, 533-68-6; $H_3CCH_2CH_2CH_3$, 106-97-8; $CH_2{=}CHCH_2CH_3$, 106-98-9; *cis*-$H_3CCH{=}CHCH_3$, 590-18-1; *trans*-$H_3CCH{=}CHCH_3$, 624-64-6; $CH_2{=}CH(CH_2)_4I$, 18922-04-8; Me_3CCH_2I, 15501-33-4; ICH_2CHMe_2, 513-38-2; $PhCH{=}CH_2$, 100-42-5; PhEt, 100-41-4; $CH_2{=}CMeCO_2Et$, 97-63-2; Me_2CHCO_2Et, 97-62-1; $CH_2{=}CHCO_2Me$, 96-33-3; $EtCO_2Me$, 554-12-1; $MeCH{=}CHCO_2Me$, 18707-60-3; *n*-$PrCO_2Me$, 623-42-7; MePrCHBr, 107-81-3; $PhCH_2CH_2Br$, 103-63-9; $PhCH_2Cl$, 100-44-7; $CH_2{=}CMeCH_2Cl$, 563-47-3; PhBr, 108-86-1.

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Electronic Structure and Reactivity of Carbynyl Cation (CR^+) Bridged Binuclear Transition-Metal Complexes

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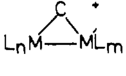
Extended Hückel calculations on carbynyl cation (CR^+) bridged binuclear transition metal complexes show that the reactivity is controlled by the LUMO of these compounds. These compounds fall into two categories according to whether or not the compound is isolobal with the cyclopropyl cation. Complexes such as $(CO)CpFe(\mu\text{-}CH)(\mu\text{-}CO)FeCp(CO)^+$, $Cp(CO)_2Mn(\mu\text{-}CR)PtL_2^+$, and $(CO)_5W(\mu\text{-}CR)PtL_2^+$, which are isolobal to the cyclopropyl cation, have a carbon-based p orbital as the LUMO. They are reactive toward the incoming nucleophiles at the carbon center. On the other hand, cationic complexes such as $CpRh(\mu\text{-}CR)(\mu\text{-}CO)RhCp^+$ and $Cp(CO)_2W(\mu\text{-}CR)AuL^+$ do not have a carbon-based LUMO and are expected to be unreactive toward nucleophiles. A least motion path for the hydrocarbation reaction is studied. Many potential candidates for the hydrocarbation reaction are suggested.

Introduction

Reactions occurring at bridging hydrocarbyl ligands have been the subject of great interest from both experimental and theoretical points of view because of their potential catalytic activity.[1] The chemistry of the compounds with a carbyne (CR) bridging two transition metals, **1**–**3**, is of special interest[2] as a model for the Fischer–Tropsch synthesis.[2a] Compounds represented by **2** are reactive at the metal center.[2c] Compounds of type **3** are reactive either at the M=C double bond without any loss of ligands or at M′ after the loss of a ligand.[2b] In **2** and **3**, the carbyne is considered as a three-electron donor. But a CR^+ bridge, as in **1**, can contribute only two electrons to the complex formation. These two participate in regular M–C σ bonds.



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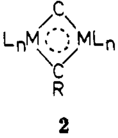

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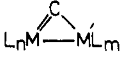

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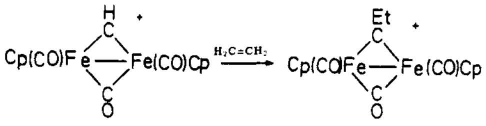
Scheme I



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5

The unsaturation at the carbon center, indicated by positive charge, leads to unusual reactivity, and a theoretical study of the system is presented in this paper.

In general, compounds of type **1** are prepared via five different routes: (1) protonating vinylidene-bridged bi-

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metallic compounds,[3] (2) dealkylating (or dealkoxylating) carbene-bridged binuclear transition metal complexes.[4] (3) reaction of alkylidyne cations $L_nM{\equiv}CR^+$ with low-valent metallic species,[5] (4) reaction of metallaallene with cationic metallic fragments,[6] and (5) protonation of 1,1-didehydrocyclopropane bridges.[7] Some compounds in which the R group (e.g. NHMe) of the bridging CR^+ unit is electron donating are also known.[8] Many compounds of type 1 are shown to be reactive toward nucleophiles.[4a,9] The reactive center is always the carbynyl carbon,[9-14] leading to an alkylidene (CR_2) bridged binuclear transition metal complex.[9-14] Deprotonation at the R group in 1 yields the vinylidene cation bridged bimetallic compound.[3a,d,10] Hydrogen migration from the R group to the bridging carbon gives the alkenyl cation bridged complex.[11] Another interesting reaction is the hydrocarbation reaction.[12] The reaction of $Cp(CO)Fe(\mu\text{-}CH)(\mu\text{-}CO)Fe(CO)Cp^+$ (4) with ethylene gives an adduct $Cp(CO)Fe(\mu\text{-}CC_2H_5)(\mu\text{-}CO)Fe(CO)Cp^+$ (5; Scheme I).[12] When the hydrogen on the carbyne bridge in 4 is replaced by any R group, such an adduct is not formed.[12,13]

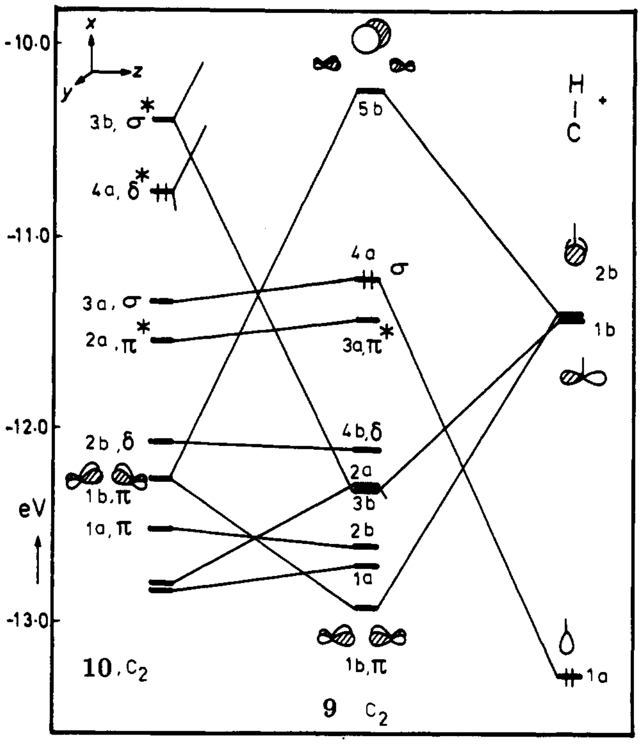

Figure 1. Interaction diagram for the construction of the molecular orbitals of $[Mn(CO)_2Cp]_2(\mu\text{-}CH)^+$ (9; C_2) from smaller fragments (CH^+) and $[Mn(CO)_2Cp]_2$, (10; C_2).

Formal electron count suggests that most of the metallic fragments in complexes of type 1 are 16-electron units. An electron from the M–C bond makes it 17 electrons, and a metal–metal bond satisfies the 18-electron count. In some examples a π delocalization in the M–C–M framework, 6, is indicated.[3c,d] An M–C double-bonded structure is suggested for heterobimetallic complexes 7.[5a] The metal electron count does not demand either a delocalized picture as in 6 or an M–C double bond as in 7. Compound 8 is

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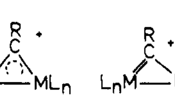

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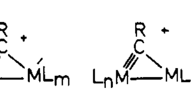

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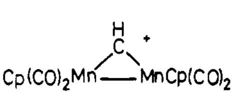
described as a complex of an alkylidyne ($L_n\equiv CR$) with another metal fragment.[15] The extent of charge on the carbynyl carbon is not clear here. Is there any π delocalization? How can we explain the reactivity of these compounds? What is the electronic origin for the hydrocarbation reaction?

Previous theoretical studies on these molecules have focused on the electronic structure of piano-stool dimers[16] and hydrogen migration reaction.[17] In this paper, we discuss our results on the electronic structure studies on compounds of type 1. The fragment molecular orbital (FMO) approach within extended Hückel theory is used to understand the molecular orbital patterns and to explain their reactivity. A least motion path is studied for the hydrocarbation reaction.

Results and Discussion

Electronic Structure of $(CO)_2CpMn(\mu\text{-}CH)MnCp(CO)_2^+$ (9). $(CO)_2CpMn(\mu\text{-}CH)Mn(CO)_2Cp^+$ (9) of C_2



9 (C_2)

11

symmetry is taken as the representative example of the bimetallic complexes with a carbynyl cation bridge, 1. Figure 1 shows the interaction diagram for the construction of the molecular orbitals of 9 from smaller fragments CH^+ and $[Mn(CO)_2Cp]_2$ (10; C_2 symmetry maintained). Details of the geometric and atomic parameters are given in the Appendix. With a d^6–d^6 electron count, the metallic fragment 10 has six of the metal d orbitals occupied. The HOMO-1 is a 3a (σ) orbital. The LUMO is a 3b (σ*) orbital with lobes directed toward the missing ligand (CH^+). Another orbital with directed lobes is 1b (π). The fragment in addition has 1a (π), 2b (δ), 2a (π*), and 4a (δ*) metal-based occupied orbitals. The availability of σ and π type orbitals makes the fragment 10 equivalent to a distorted ethylene. The isolobal analogy[18] also supports this idea.

Figure 1 shows the strong interaction between the 1b orbital of fragment 10 and the 2b orbital of CH^+ leading to a carbon-based LUMO. The 1a orbital of CH^+ slightly destabilizes the 3a (σ) orbital of fragment 10. The 4a (δ*) orbital of 10 is pushed high up in energy into the unoccupied region. The metal–carbon σ bond formation is due to the interaction of 3b (LUMO) of 10 with the in-plane p orbital of the CH group. The 4a orbital in 9 corresponds to the M–M σ bond. The 1b orbital of 9 is the bonding combination of the π orbital of 10 and p of carbon, which may support the proposed cyclic π system in the molecule.[3c,d] However, the 1b orbital of 9 is mostly based on the two metals, which is cancelled by the 3a (π*) orbital. This indicates that the M–C–M π delocalization, if any, is very small and cannot be similar to the delocalization in 2. Metal-based M–M σ, π, π*, δ, and δ* orbitals are occupied in 9, resulting in only a M–M single bond. An interesting aspect of this interaction diagram is the presence of an almost pure carbon p (5b) orbital as the LUMO, 11 (Figure 1). 9 is isolobal to the cyclopropyl cation, $C_3H_5^+$.

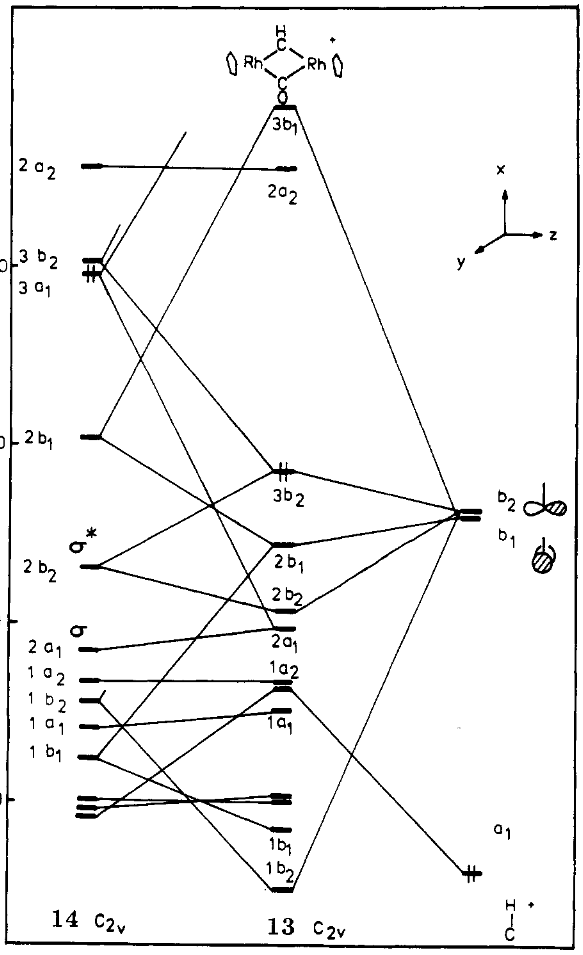


Figure 2. Interaction diagram for the construction of the molecular orbitals of $CpRh(\mu\text{-}CO)(\mu\text{-}CH)RhCp^+$ (13; C_{2v}) from the smaller fragments CH^+ and $CpRh(\mu\text{-}CO)RhCp$ (14; C_{2v}).

The reactivity of the complexes of type 1 should arise from this easily accessible p orbital as LUMO. The electronic structure and reactivity of piano-stool dimers bridged by CH^+ have been reported previously.[16] It was pointed out that the presence of a carbon p orbital as the LUMO in $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}CH)Fe(CO)Cp^+$ (4) is responsible for its electrophilicity. Nonavailability of a carbon-based p orbital as LUMO is shown to be responsible for the unreactivity of $CpFe(\mu\text{-}NO)_2(\mu\text{-}CH)FeCp^+$ toward nucleophiles.[16] In tune with this, $[Mn(CO)_2Cp]_2(\mu\text{-}CH)^+$ (9) should also be highly reactive at the carbon center toward nucleophiles. $[Mn(CO)_2Cp]_2(\mu\text{-}CMe)^+$ is found in solution as an intermediate in vinylidene interconversion on the metallic template,[3a] indicating the high reactivity at the carbon center in these complexes.

$[Fe(CO)Cp]_2(\mu\text{-}CO)(\mu\text{-}CH)^+$,[4b] $[Fe(CO)Cp]_2(\mu\text{-}CO)(\mu\text{-}CCH_3)^+$,[3g] $[Fe(CO)_4]_2(\mu\text{-}CCH_3)^+$,[4d] $[RuCp(CO)]_2(\mu\text{-}CO)(\mu\text{-}CMe)^+$,[3n,z] $[FeCp]_2(\mu\text{-}dmpm)(\mu\text{-}CO)(\mu\text{-}COMe)^+$,[4g] and $[CpCo(CO)]_2(\mu\text{-}CMe)^+$[4f] are all isoelectronic with 9 and

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[15] (a) Carriedo, C. A.; Howard, J. A. K.; Stone, F. G. A.; Went, M. J. *J. Chem. Soc., Dalton Trans.* **1984**, 2545. (b) Green, M.; Howard, J. A. K.; James, A. P.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 61. (c) Baumann, F.-E.; Howard, J. A. K.; Musgrove, R. J.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1988**, 1879.

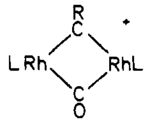
[16] (a) Bursten, B. E.; Cayton, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 8241. (b) Bursten, B. E.; Cayton, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 6503. (c) Bursten, B. E.; Cayton, R. H. *Polyhedron* **1988**, *7*, 943.

[17] (a) Silvestre, J.; Hoffmann, R. *Langmuir* **1985**, *1*, 621. (b) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 7461. (c) Pinhas, A. R.; Albright, T. A.; Hofmann, P.; Hoffmann, R. *Helv. Chim. Acta* **1980**, *63*, 29.

[18] (a) Hoffmann, R. *Angew.* Chem., *Int. Ed. Engl.* **1982**, *21*, 711. (b) In the counting of electrons around the metals in finding the isolobal analogs, the bridging carbonyl is considered as donating one electron to each metal.

isolobal to the cyclopropyl cation ($C_3H_5^+$). Extended Hückel calculations, not detailed here, show that the electronic structure of these compounds is similar to that of **9**. The LUMO of these compounds is a carbon-based p orbital, and most of them are reported to be reactive toward the incoming nucleophiles.[3]

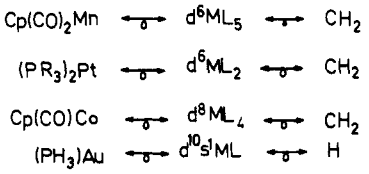
Electronic Structure of (C_5Me_5)Rh(μ-C(C_6H_4Me-4))(μ-CO)Rh(C_5Me_5)$^+$ (12).[4i] CpRh(μ-CH)(μ-CO)RhCp$^+$ (**13**) is taken as a model for **12**. Figure 2 shows the interaction diagram for the construction of the molecular orbitals of **13** (C_{2v}) from smaller fragments, CH$^+$ and CpRh(μ-CO)RhCp (**14**, C_{2v}). In **14**, apart from the ligand-based orbitals (not labeled), the following metal-based orbitals are occupied: $1b_1$ (δ), $1a_1$ (δ), $1b_2$ (δ^*), $1a_2$ (δ^*), $2a_1$ (σ), $2b_2$ (σ^*), $2b_1$ (π), and $3a_1$ (π). The HOMO is the $3a_1$ (in-plane π orbital) between the two metals. The LUMO is the $3b_2$ (in-plane π^* orbital). The $2a_2$ (out-of-plane π^*) orbital is the LUMO+1. In **14**, both $2a_1$ (σ) and $2b_2$ (σ^*) are occupied, indicating the absence of any M–M σ bond. However, there is some bonding interaction because of the positive overlap of metal d orbital lobes directed away from the M–M axis. The M–M Mulliken overlap population is 0.112. Two M–M π orbitals, $2b_1$ and $3a_1$ are occupied. Interaction of fragment **14** with CH$^+$ leads to **13**. The major interactions are between the $3b_2$ (π^*) orbital of **14** and the b_2 orbital of CH$^+$ leading to M–C σ bond formation. The resultant $3b_2$ of **13** is slightly pushed up by the interaction with the $1b_2$ and $2b_2$ orbitals of **14**, and the $3a_1$ orbital of **14** is pushed up beyond the frontier region of **13**. In contrast, the $3b_2$ orbital of **13** is occupied. The a_2 orbitals do not find a match among the orbitals of CH$^+$ and remain untouched, and $2a_2$ (M–M π^*) of **14** becomes the LUMO $2a_2$ of **13**. The p orbital of CH$^+$ stabilizes the $2b_1$ orbital of **14**. The corresponding antibonding combination $3b_1$ is the SLUMO (second LUMO) in **13**, mainly concentrated on the p orbital of carbon. Orbitals $1a_1$, $2a_2$, and $3a_1$ of **14** interact with the $1a_1$ orbital of CH. The lowest of these is not shown in the diagram. The highest of these is very high in energy and is also not shown. All the bonding and antibonding interactions of the metal–metal axis are occupied, $1b_2$ (δ^*), $1b_1$ (δ), $1a_1$ (δ), $1a_2$ (δ^*) $2a_1$ (σ), $2b_2$ (σ^*), $2b_1$ (π), and $3b_2$ (π^*). Therefore, the proposed bond order of 2 for **13** cannot be true.[19] The extent of the bonding and antibonding interaction is not equal, as indicated by the M–M Mulliken overlap population in **13** (0.064) indicating a weak M–M interaction. The HOMO–LUMO gap is large (1.72 eV), which accounts for the high stability of the compound.[4i] The $1b_1$ orbital of **13** is the bonding combination of the π orbital of **14** and the p orbital leading to a proposal of cyclic π delocalization. In view of the charge, compound **12** may be expected to react with nucleophiles to give an alkylidene (CR_2) bridged bimetallic system.[4i] Our analysis shows that the carbon-based p orbital is the SLUMO in **13**, very high in energy, indicating that the reactivity of **12** with nucleophiles may not be very high.[20] **12** is isolobal to the cyclopropenyl cation, $C_3H_3^+$, but not to the cyclopropyl cation, $C_3H_5^+$.[18]



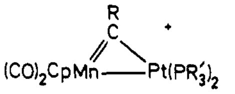
12 (L = C_5Me_5; R = C_6H_4 Me-4)

13 (L = C_5H_5; R = H; C_{2v})

Scheme II



Electronic Structure of Cp(CO)$_2$Mn(μ-C(C_6H_4Me-4))Pt(PH$_3$)$_2^+$ (15).[5a] Two different electron distributions are proposed in the cationic complexes with a CR bridge on a heterobimetallic template.[5] One has a metal carbon double bond, **7**, where the charge is suggested to be localized on the ML_n unit. The other has a metal–carbon triple bond where the charge is suggested to be localized on $M'L_m$ (**8**). In analogy to compounds of type **3**,[2] complexes of type **7** should be reactive toward a carbene to give an adduct (because of the M–C double bond). However, no report of such a reaction is available in literature. Instead these compounds show exceptional reactivity toward the nucleophiles at the carbon center,[9e] very much similar to compounds of type **1**. To clearly understand the bonding and reactivity of these compounds, we studied Cp(CO)$_2$Mn(μ-CH)Pt(PH$_3$)$_2^+$ (**16**), a representative of compounds of type **7**. The metallic fragments MnCp(CO)$_2$ and Pt(PH$_3$)$_2$ in **16** are isolobal to CH$_2$, and the compound is isolobal to the cyclopropyl cation (Scheme II).



15 (R = C_6H_4Me-4; R' = H)

16 (R = R' = H)

Extended Hückel calculations suggest that the electronic structure of compound **15** is very much similar to that of **9** in the frontier range. Small differences appear due to the hetero nature of the metallic template. The LUMO is a purely carbon-based p orbital which has an antibonding interaction with the δ orbital of the M–M axis, **11**. In Cp(CO)$_2$Mn$\equiv$CR$^+$, only Mn–C σ and inplane π orbitals are occupied. The out-of-plane π orbital between Mn and C is unoccupied. The interaction diagram between Cp(CO)$_2$Mn$\equiv$CR$^+$ and PtL$_2$ is not reproduced because it gives no further clues other than the standard M–C and M–M bonding interactions. From the nature of the LUMO, the observed reactivity toward nucleophiles can be supported. Since no orbital corresponding to the out-of-plane Mn–C π bond is occupied, an Mn$=$C double bond should not be expected. The charge matrix shows that the carbon is positively charged. This indicates that structure **7** is not a correct representation of these compounds—instead structure **1** is best suited to represent these examples. The MO pattern of (CO)$_5$W(μ-CR)Pt(PH$_3$)$_2^+$[5a] also is similar to that of **15**. In Cp(CO)$_2$Mn(μ-C(C_6H_5Me-4))Pt(PMe$_3$)$_2^+$,[5b] a partial bridging interaction between one of the carbonyls on Mn and the metal Pt is reported.[5a,b] The overlap population between Pt and the C(O) close to it is positive (0.024), indicating a very weak semibridging Pt–C interaction.

Electronic Structure of Cp(CO)$_2$W(μ-CH)Au(PH$_3$)$^+$ (17). Cp(CO)$_2$W(μ-C(C_6H_4Me-4)Au(PPH$_3$)$^+$[15] is an ex-

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[19] M–M bonding distances observed in several compounds indicate single or double condition order, but the MO pattern precludes the possibility of an M–M bonding interaction. Examples are given in the following papers. (a) CpM(μ-NO)$_2$MCp: Bottomly, F. *Inorg. Chem.* **1983**, *22*, 2656. (b) R$_2$Si(μ-O)$_2$SiR$_2$: Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 822.

[20] This is in accordance with the experimental findings: Professor P. A. Chaloner, personal communication.

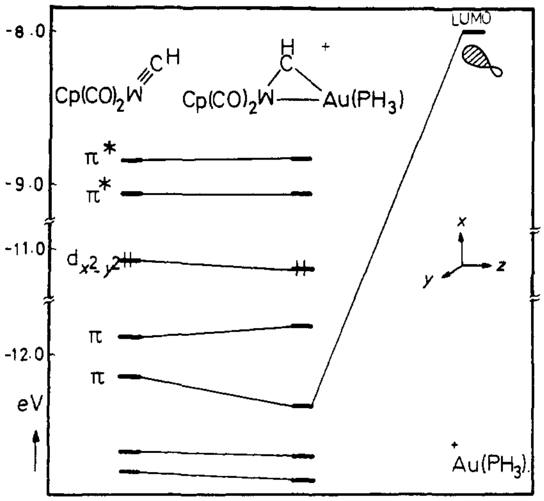
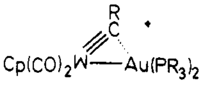


Figure 3. Interaction diagram for the construction of molecular orbitals of $Cp(CO)_2W(\mu\text{-}CH)Au(PH_3)^+$ (17) from smaller fragments $Cp(CO)_2W{\equiv}CH$ and $Au(PH_3)^+$. The occupied orbitals of $Au(PH_3)$ are very low in energy (the HOMO is at −14.28 eV).

ample of compounds of type 8 for which two different representations, one with a partial Au–C single bond, 18,



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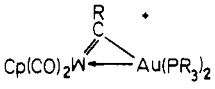
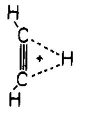


19

and the other in which the Au atom donates electrons to the W atom, with a regular Au–C bond, 19, are suggested.[15b] The molecular orbitals of 17 are constructed from those of the fragments $(CO)_2CpW{\equiv}CH$ and $Au(PH_3)^+$ (Figure 3). The energies of the HOMO and LUMO of $Au(PH_3)^+$ are not close to the energies of the frontier orbitals of $Cp(CO)_2W{\equiv}CH$. The HOMO is very low in energy and is not shown. The fragment $(CO)_2CpW{\equiv}CH$ has a σ and two π occupied orbitals along the W–C axis. The LUMO is a W–C π^* orbital. The interaction diagram clearly shows that there is no significant interaction between the two fragments. The in-plane π orbital of $Cp(CO)_2W{\equiv}CH$ is only slightly stabilized because of its interaction with the σ (LUMO) orbital of fragment $Au(PH_3)$. The in-plane W–C π^* orbital is not affected because of the absence of the corresponding metal-based orbital on $Au(PH_3)$. The large W–C–R angle (164°) in 17 suggests the absence of significant rehybridization at the carbon center in forming 17. The W–Au and Au–C overlap populations of 0.084 and 0.343 indicate some bonding interaction. The situation here is reminiscent of the bonding pattern in vinyl cations, $C_2H_3^+$ (20).[21] The Au–C overlap population



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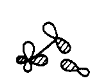
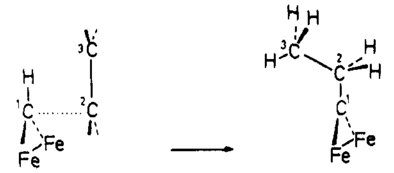


21

of 0.343 is arising mostly from the MO shown in 21. $Cp(CO)_2W$ is isolobal to CH, and $Au(PH_3)$ is isolobal to H. Hence, 17 is isolobal to the bridged vinyl cation 20. Compound 17 should not be considered as a part of the CH^+-bridged bimetallic complexes, because the charge in this molecule is more concentrated on Au rather than the carbon.

Scheme III



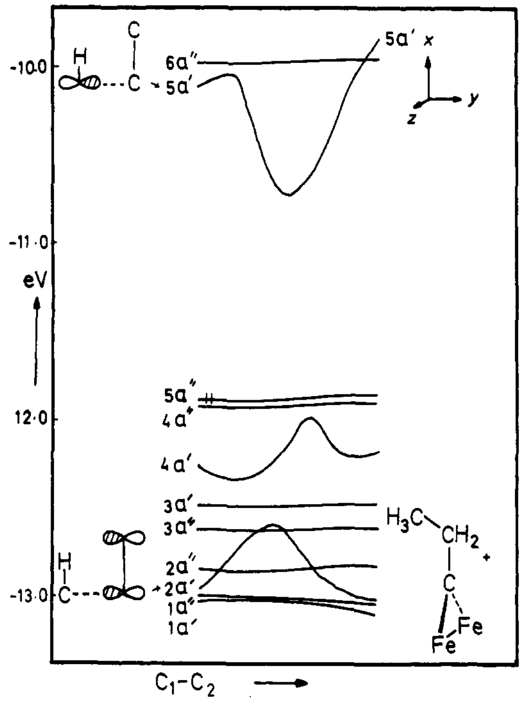


Figure 4. Walsh diagram showing the least motion pathway for the hydrocarbation reaction between $Cp(CO)Fe(\mu\text{-}CO)Fe(CO)Cp^+$ (4a; C_s) and ethylene (C_s symmetry maintained).

The above discussion suggests that carbynyl cation bridged compounds which are isolobal to the cyclopropyl cation ($C_3H_5^+$) have their LUMO on the p orbital of the bridging carbon. These compounds are reactive toward the nucleophilic attack at the carbon center. The carbynyl cation bridged compounds which are not isolobal to cyclopropyl cation may not be reactive toward nucleophilic attack because of the absence of p orbital as the LUMO. Hence, $[Fe(CO)Cp]_2(\mu\text{-}CO)(\mu\text{-}CH)^+$, $[Fe(CO)_4]_2(\mu\text{-}CMe)^+$, $[Co(CO)Cp]_2(\mu\text{-}CMe)^+$, $Cp(CO)_2Mn(\mu\text{-}CR)PtL_2^+$, $(CO)_5W(\mu\text{-}CR)PtL_2^+$, etc. but not $CpRh(\mu\text{-}CR)(\mu\text{-}CO)RhCp^+$, $Cp(CO)_2W(\mu\text{-}CR)AuL^+$, $CpFe(\mu\text{-}CH)(\mu\text{-}NO)_2FeCp^+$, etc. are expected to be electrophilic at the bridging carbon center.

Hydrocarbation Reaction. Reaction of $Cp(CO)Fe(\mu\text{-}CH)(\mu\text{-}CO)Fe(CO)Cp^+$ (4) with ethylene gives $Cp(CO)Fe(\mu\text{-}CCH_2CH_3)(\mu\text{-}CO)Fe(CO)Cp^+$ (5) (Scheme I).[12] This reaction is found to be very general and takes place with every possible alkene. $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}CEt)Fe(CO)Cp^+$ (5) does not react with alkenes. Hence, it was proposed that a C–H addition to ethylene is responsible for the reaction.[12] It can be expected that the C–H bond cleavage can be possible only when ethylene (or alkene) donate its π electrons to the C–H σ^* orbital of the CH^+ bridge and when C–H σ electrons are donated to the C–C π^* orbital of ethylene. But the LUMO of 4 is only a carbon-based p orbital and there is no interaction between carbon and hydrogen in this orbital. To understand the electronic origin of the hydrocarbation reaction, calculations are performed on the reaction path.

A least motion path for the hydrocarbation reaction where one carbon of the ethylene attacks the bridging carbon of *cis*-$Cp(CO)Fe(\mu\text{-}CH)(\mu\text{-}CO)Fe(CO)Cp^+$ (4a) is

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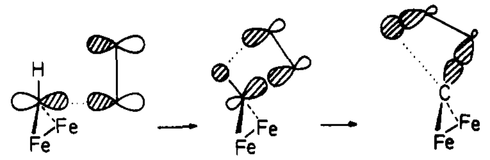
[21] (a) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649. (b) Jemmis, E. D.; Sarma, K. S.; Pavan Kumar, P. N. V. *J. Mol. Struc.* (*THEOCHEM*) **1985**, *121*, 305.

Scheme IV

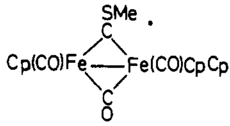


given in Scheme III (C_s symmetry is maintained).[22] Extended Hückel calculations are performed along the proposed reaction path to construct an orbital correlation diagram (Figure 4). The variation in the sum of the one-electron energy shows a barrier of 1.9 eV. The reaction is formally allowed but Figure 4 shows strong avoided crossings involving the 2a′, 4a′, and 5a′ orbitals. Detailed analysis shows that these avoided crossings are due to the donation of ethylene π electrons to the C–H σ^* orbital, as shown in Scheme IV, finally leading to the formation of the C_1–C_2 and C_3–H bonds and cleavage of the C_1–H bond. The ethylene π orbital in 2a′ goes up in energy due to the decrease in the π interaction. The 5a′ orbital initially increases in energy due to the development of a C–H antibonding (σ^*) interaction and later decreases due to the decrease in the C–H σ^* interaction as the distance between C and H increases. The 4a′ orbital represents the transfer of C–H σ electrons to the C–C π^* orbital. The avoided crossing gives rise to the observed energy barrier (1.9 eV). EH calculations on the hydrocarbation reaction using **4** (**4** has trans Cp rings, with no symmetry in the reaction path) indicate a barrier of 2.0 eV. Thus, our calculations support the concerted reaction path proposed by Casey et al.[12d]

A similar reaction is not possible when hydrogen is replaced by an alkyl group.[12,13] The LUMO in (CO)CpFe(μ-CO)(μ-CCH$_3$)Fe(CO)Cp$^+$ (**22**) is also a carbon-based p orbital. However, it has a π^* interaction with a pseudo p orbital of the CH$_3$ group. As the ethylene approaches the carbynyl carbon, no C–Me σ^* interaction is observed in the frontier range. Hence, donation of π electrons from the ethylene to the C–Me σ^* orbital of **22** is not possible, which denies the adduct formation necessary for the reaction of **22** with ethylene.

From the above discussion, it is clear that alkenes can react at the carbynyl carbon only if the substituent on the carbynyl carbon is hydrogen. Compounds [Fe(CO)$_4$]$_2$(μ-CH)$^+$, [Cp(CO)$_2$Mn]$_2$(μ-CH)$^+$, (CO)$_2$CpMn(μ-CH)PtL$_2$$^+$, (CO)$_5$W($\mu$-CH)PtL$_2$$^+$, etc., which are isolobal to the cyclopropyl cation, have electronic structures similar to that of **4**. They are expected to demonstrate hydrocarbation reactions. Since the hydrocarbation reaction is an interesting reaction with potential catalytic use, the preparation of all the CH$^+$-bridged compounds which are isolobal to the cyclopropyl cation should be attempted and tested for the hydrocarbation reaction.

Carbyne Radical Bridges on Bimetallic Templates. Some radical species are identified with the help of ESR spectra in compounds where a carbyne group bridges two metals.[4f,23,24] The well-characterized examples are [Cp(CO)Fe]$_2$(μ-CO)(μ-CSMe)$^\bullet$ (**23**)[23] and [Cp(CO)Co]$_2$(μ-CMe)$^\bullet$ (**24**).[4f,24] The Fe system, **23**, is very close to **4** except for the replacement of H by SMe group and for the extra electron. The electronic structure is very much similar to that of **4**. The extra electron in **23** goes into the LUMO (i.e. **11**). Since **11** is antibonding between the p orbital of carbon and the δ orbital of the metallic template, no delocalization of this extra electron in the M–C–M π framework should be expected. The chemical reactivity of these radicals is not studied in detail. Reaction of **23** with another radical ($^\bullet$Seph) gives a carbene-like bridging unit.[23] This supports the idea that the odd electron in **23** is localized on carbon only. Co(CO)Cp is isolobal to CH$_2$. Thus, **24** is supposed to have an electronic structure similar to that of **23**. Both **23** and **24** are isolobal to the cyclopropyl radical.



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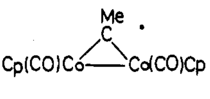

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Conclusions

The reactivity of the compounds of type **1** is controlled by their LUMO. Nucleophilic attack at the carbon center is triggered by the LUMO in those compounds which are isolobal to the cyclopropyl cation. Extended Hückel calculations on various compounds of type **1** suggest that the CR bridge in Cp(CO)Fe(μ-CH)(μ-CO)Fe(CO)Cp$^+$, (CO)$_4$Fe(μ-CR)Fe(CO)$_4$$^+$, Cp(CO)$_2$Mn($\mu$-CR)PtL$_2$$^+$, (CO)$_5$W($\mu$-CR)PtL$_2$$^+$, etc., which are isolobal to the cyclopropyl cation, is electrophelic. (C$_5$Me$_5$)Rh(μ-CR)(μ-CO)Rh(C$_5$Me$_5$)$^+$, CpFe(μ-CH)(μ-NO)$_2$FeCp$^+$, and Cp(CO)$_2$W(μ-Cr)Au(PR)$_3$$^+$ are not isolobal to the cyclopropyl cation and are not expected to be electrophilic at the carbynyl carbon center. The hydrocarbation reaction of (CO)CpFe(μ-CO)Fe(CO)Cp$^+$ with ethylene adopts a possible least motion pathway which allows the donation of ethylene π electrons to the C–H σ^* orbital. **17** is not a CR$^+$-bridged compound. Compounds which have a methylidyne cation (CH$^+$) bridge on binuclear transition metal complexes and which are isolobal to the cyclopropyl cation are expected to be very good reagents for the hydrocarbation reaction.

Acknowledgment. B.V.P. thanks the CSIR, New Delhi, for a Senior Research Fellowship. This research was partially funded by the Department of Science and Technology, New Delhi.

Appendix

The geometries adopted in the model calculations are based upon the known complexes wherever possible: Mn–Mn, 2.76 Å; Mn–C, 2.01 Å; C–H; 1.08 Å; Fe–Fe, 2.50 Å; Fe–C; 1.86 Å; Ru–Ru, 2.62 Å; Ru–C; 1.91 Å; Rh–Rh, 2.51 Å; Rh–C, 1.92 Å; Rh–C(O), 1.96 Å. The Walsh diagram for the hydrocarbation reaction in Figure 4 is described by a least motion between the bridging CH of **4a** and ethylene. The initial distance between C(H) of **4a** and the carbon of ethylene closest to it is 3.00 Å. The reaction path is defined as the decrement in this distance. Other necessary changes are made to get the final compound **5**. C_s symmetry is maintained. Distances in **16**, are as follows: Pt–Mn, 2.63 Å; Pt–C, 1.97 Å; Mn–C, 1.83 Å. Distances in **17** are as follows: W–Au, 2.72 Å; W–C, 1.81 Å; Au–C, 2.21 Å.

OM910470P

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[22] Hydrocarbation reaction is reported with **4**, which has a trans arrangement of the Cp rings with respect to the Fe–Fe axis. To maintain C_s symmetry, **4a** is chosen here (see Appendix).

[23] (a) Schroeder, N. C.; Angelici, R. *J. Am. Chem. Soc.* **1986**, *108*, 3688. (b) Asturc, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 643.

[24] Koenig, T. W.; Hay, B. P.; Finke, R. G. *Polyhedron* **1988**, *7*, 1499.